The Photophysics of Some Styrenes

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Summary The measurement of fluorescence lifetimes, fluorescence quantum yields and isomerization quantum yields for a series of sytrenes has shown that although rotation about the double bond is an important non-radiative process, other non-radiative processes which are structure dependent make important contributions.

STYRENES are the simplest conjugated olefins which exhibit both photochemical geometric isomerization and luminescence. Moreover, since we now know a great deal about the photophysics of benzene and some of its alkyl derivatives, the styrenes are attractive molecules for the study of photochemical geometric isomerization and the competing non-radiative relaxation modes of excited olefins.[1–4]

The Table shows the fluorescence quantum yields and fluorescence lifetimes of the styrenes studied, together with the values of k_{NR} and k_R obtained from this experimental data. The measured non-radiative rate constant for the S_1 state may be divided into three contributing processes;[1,2] (i) intersystem crossing, (ii) internal conversion—involving rotation (or partial rotation in the case of cyclic systems) about the olefinic double bond, and (iii) other internal conversion pathways. The striking feature about the data in the Table is the relationship between the number of C–H bonds on carbon atoms directly attached to the olefinic double bond and k_{NR}. Thus, styrene and t-butylstyrene with no such C–H bonds have values of k_{NR} considerably lower than the k_{NR} values for the monomethylstyrenes. The latter, in turn, have lower non-radiative rate constants than α,β-dimethylstyrene and 1-phenylcyclohexane.

On theoretical grounds,[1] it is unlikely that the relaxation mode effected by the presence of the α C–H bonds is intersystem crossing. This is supported by the lack of correlation between k_{NR} and the singlet–triplet splittings in these styrenes,[5] and thus the trends observed are due to the effects on the double bond rotation (leading to isomerization in the case of acyclic systems) or due to the participation of some other internal conversion process. Hui and Rice[1] have analysed the singlet state isomerization pathway of styrene in terms of a theory[6] which assumes that most of the excess energy available on crossing from the potential energy surface of the S_1 state to an isoenergetic level in the ground state is taken up in torsional motion, and thus the ratio of the k_{NR} (isomerization) values for styrene, [$^2H_1$]-*trans*-β-styrene and [$^2H_8$]-styrene is related to the density of free rotor stases in S_0, the ground state. That this analysis cannot account for our observations is evident.

In order to probe further the relative importance of rotational relaxation and other non-radiative relaxation processes in styrenes, we have measured the quantum yields of isomerization for a number of styrenes. The results provide support for our hypothesis of a non-rotational relaxation in styrenes with hydrogen atoms on carbons α to the double bond playing a crucial role. ϕ_{t-c} [β-t-butylstyrene (**1**)] = 0·38; ϕ_{t-c} [β-methylstyrene (**2**)] = 0·22.

Photophysical parameters of some styrenes in cyclohexane

Compound	ϕ_F[a]	τ[b]/ns	$k_R \times 10^{-7}$ s^{-1}	$k_{NR} \times 10^{-7}$ s^{-1}
Styrene[c]	0·15	12·5	1·20	6·7
[d]	—	11·4		
[e]	0·36	20·3	1·80	3·2 (gas phase)
trans-β-t-Butylstyrene	0·155	12·6	1·25	6·7
trans-β-Methylstyrene	0·028	2·4	1·15	40·5
cis-β-Methylstyrene	0·0045	2·7	0·17	37·0
α-Methylstyrene	0·028	2·7	1·05	36·0
E-α, β-Dimethyl-styrene ..	0·014	1·9	0·700	52·0
1-Phenylcyclohexene	0·018	1·8	1·00	54·5

[a] Excitation wavelength 265 nm. However, for α-methylstyrene ϕ_F was found to be independent of excitation wavelength (250—285 nm). [b] Excitation wavelength 254 nm. [c] This work. [d] See, 'Fluorescence Spectra of Aromatic Molecules,' 2nd edn., I. B. Berlman, Acad. Press, 1971, p. 174. [e] M. H. Hui and S. A. Rice, *J. Chem. Phys.*, 1974, **61**, 883.

Making two reasonable assumptions, (a) that intersystem-crossing is relatively unimportant in styrenes[7] (but see later) and (b) that following rotation from the planar singlet state, the twisted styrene will relax with equal efficiency to the *cis* and *trans* ground states, *i.e.* $2k_{isom.} = k_{rot.}$,[8] and using the relationship $k_{isom} = \phi_{t-c}\tau_F^{-1}$ then one can calculate that $k_{rot.}$ (**1**) = $6\cdot0 \times 10^7$ s^{-1}, and $k_{rot.}$

(2) = $17{\cdot}5 \times 10^7\,s^{-1}$. Thus the rotational relaxation process in **(1)** can, to a good approximation, account for all the non-radiative decay from the S_1 state, while for **(2)** some other non-radiative process(es) having a rate constant of $13 \times 10^7\,s^{-1}$ is present. The difference between $k_{rot.}$ for **(1)** and **(2)** is intriguing and is perhaps larger than might have been expected on the grounds of steric bulk.

A clue to the possible nature of an internal conversion involving the α C–H bond comes from the observation that phenylcyclopropanes are formed on prolonged irradiation of some alkyl styrenes and the related 1,1-diphenylethylenes.[9] The cyclopropanes are considered to be formed by a 1,2 migration of hydrogen (or alkyl) followed by cyclization. Thus a state involving partial bonding of the migrating group to the α-carbon and the adjacent olefinic carbon, which may relax to the ground state olefin or (less efficiently) give a cyclopropane, seems possible and has analogies in olefin and ketone photochemistry.

The existence of a non-radiative relaxation route, not involving rotation about the double bond is qualitatively supported by other isomerization quantum yield measurements.†

Finally, the effect of structure in the pair α,β-dimethylstyrene, 1-phenylcyclohexene provides evidence that the cyclohexene ring exhibits no barrier to rotation about the double bond in the excited state. Thus, rotation may proceed to the point where relaxation to the twisted ground state potential energy surface is possible. This has important implications for the bimolecular photochemical reactions of arylcyclohexenes and perhaps other arylcycloalkenes.

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† It should be pointed out that the arguments presented will still hold even if the non-radiative process in question is intersystem-crossing, since it has been demonstrated that in solution the quantum yield of triplet sensitized isomerization (c → t or t → c) is 0·5 for **(2)**,[4] *i.e.* ϕ rotation = 1·0. If intersystem crossing were the major route, the value calculated as $k_{rot.}$ for the internal conversion pathway becomes k_{isc} for the intersystem crossing pathway.

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[6] W. M. Gelbart, S. A. Rice, and K. F. Freed, *J. Chem. Phys.*, 1970, **52**, 2460.

[7] H. E. Zimmerman, K. S. Kamm, and D. P. Werthermann, *J. Amer. Chem. Soc.*, 1074, **96**, 7821.

[8] Of the very many singlet and triplet state isomerization processes of olefins studied, this generalisation is usually found to be valid. See J. Saltiel, J. D'Agostino, E. D. Megarity, L. Metts, K. R. Neuberger, M. Wrighton, and O. C. Zafiriou, *Org. Photochem.*, 1973, **3**, 1. Moreover, we have tested the assumption by measuring ϕ_{c-t} **(2)** and, within experimental error, the decay ratio was found to be unity.

[9] Since t-butylstyrene is known to undergo a rearrangement, presumably with low quantum efficiency, to give a trimethylphenylcyclopropane it is not expected that $k_{rot} = \Sigma\, k_{NR}$. H. Kristinsson and G. W. Griffin, *J. Amer. Chem. Soc.*, 1966, **88**, 378; G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Letters*, 1965, 2951.